CHAPTER 3

3. PERIODICAL AND CLUSTER CALCULATIONS ON EXPERIMENTAL CRYSTALLINE GEOMETRY

In this chapter we will apply single point periodical calculations on experimental crystalline geometry to the crystal of benzoquinone, compare the results to single point cluster calculations at different levels of theory, and consider the applicability of this approach to urea and thiourea.

3.1 Crystalline benzoquinone.

Para-benzoquinone forms stable crystals with a melting point of $116°$ C. A plane from the crystal structure is shown in Figure 3.1. All stabilizing interactions between the nearest neighbors within the plane are C-H...O hydrogen bonds. To understand the nature and the strength of the individual hydrogen bonds involved in the intermolecular interactions leading to crystal formation, and their cooperative effects, we applied *ab initio* cluster and periodical calculations to *para*-benzoquinone.

We performed *ab initio* calculations using the GAUSSIAN 94 and both CRYSTAL 92 and CRYSTAL 95 (CRYSTAL) suites of programs. Specific to the periodical calculations is that the coulomb and exchange integrals are evaluated
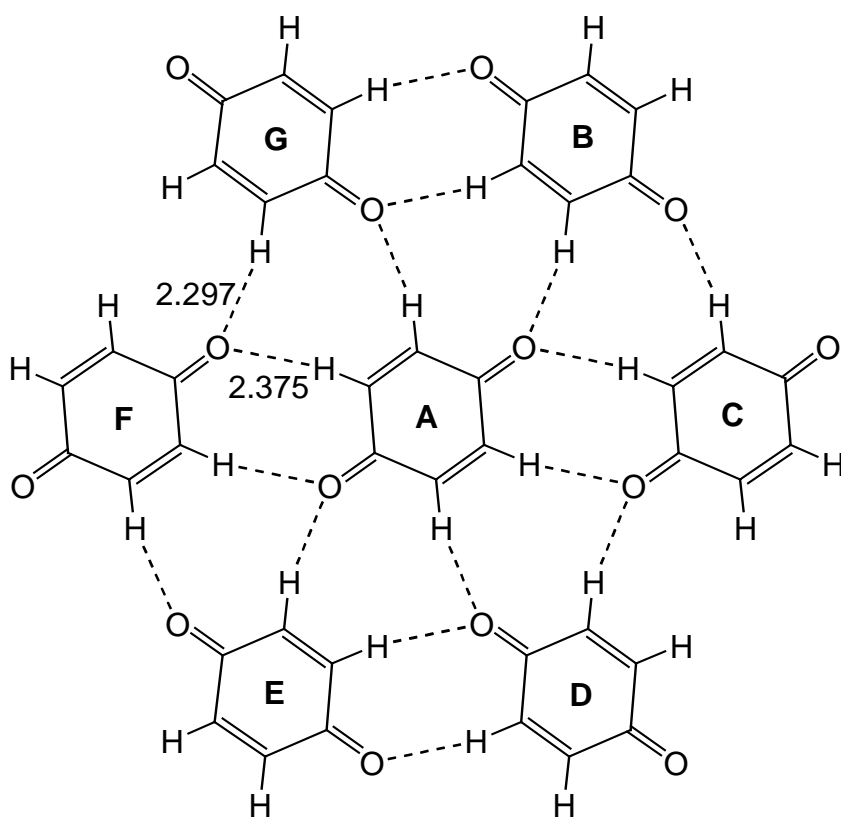
Figure 3.1. Seven molecules within a plane taken from the experimental crystal structure of *para*-benzoquinone.

exactly only when the overlap is larger then a given threshold and estimated from multipolar expansions by the Ewald method outside this inner zone.[1] Corresponding threshold levels (including coulomb overlap, coulomb penetration, and exchange overlap tolerances) were set to 10^{-6}, 10^{-8}, and 10^{-6}, respectively. Other tolerances (pseudo overlap) refer to different terms in the exchange summation series in reciprocal space and were left at their default levels (10^{-6} and 10^{-12}). Convergence criteria were 10^{-5} on eigenvalues and 10^{-6} on total energy. We found these values for

tolerances and convergence to be necessary to make the CRYSTAL calculations consistent with GAUSSIAN 94 calculations on identical clusters. We changed the conversion factor between Ångstroms and Bohrs in CRYSTAL 92 (where it is given to five places) to the more precise value used in GAUSSIAN 94. Without this change, there were slight (about 0.6 kcal/mol) differences in the internuclear repulsions for the monomer. GAUSSIAN 94 uses six d-functions as the default for the polarization functions, while CRYSTAL uses only five. The 6-21G** calculations performed with GAUSSIAN 94 used the (non-default) value of five d-orbitals.

We used GAUSSIAN 94 to calculate aggregates of from 1 to 7 *para*-benzoquinone molecules. Both Hartree-Fock and the density functional theory were used with the 6-21G** and D95* basis sets. The DFT calculations employed the B3LYP and B3PW91 functionals. In addition, we used the AM1 semiempirical method[2] to calculate the aggregates for comparison. This method has been shown to give accurate results for H-bonds other than those involving O-H...O[3] and C-H...O interactions in dimeric H-bonding interactions,[4] The method also seems to give reasonable results for aggregate calculations,[5] although no energetic comparisons for these specific interactions are available. MP2 calculations of two stacking interactions were also performed. These were limited to dimers.

We prefer to use neutron diffraction studies as input to our calculations, as these directly provide the positions of the hydrogen atoms. However, no neutron diffraction studies of *para*-benzoquinone crystals have been reported. The present calculations use the experimental crystal geometry taken from the low temperature

(-160" C) X-ray diffraction study (R 0.074).[6] An earlier X-ray diffraction study at

room temperature had been reported.[7] The coordinates were taken directly from the

Cambridge Crystallographic Data Base.[8] The positions of the H-atoms were fixed at

1.08 Å from the carbon atoms in the crystal structure. *para*-Benzoquinone crystallizes

with a unit cell containing two molecules in space group $P2_1/a$. Both molecules of the

unit cell provided the repeating unit for 3D- (crystal) and 2D- (slab) calculations. One

molecule is sufficient for the repeating unit in one of the 1D-chains, while two

molecules are necessary for the other two (equivalent) chains. One should note that the

H-bonding sheets in the crystal slightly deviate from planarity.

The counterpoise[9] corrections to the basis set superposition error were

performed differently in the aggregate and periodic calculations. For the aggregates,

the counterpoise (CP) correction was evaluated from the calculation of each

monomeric unit in the presence of the ghosts of all the others. As it was described in

the Section 2.3, the counterpoise correction for the periodic calculation is usually done

using cluster calculations of the molecule in the presence of a limited number of

ghosts, representing the nearest atoms of other molecules. We found this approach

unsatisfactory. Instead, we considered all the ghosts located closer than a certain

distance to any atom of the monomeric unit. Gradually increasing this distance, we

monitored the change in the CP-correction. The distance of 4 Å was chosen as a

compromise between disk space and precision. CP-correction is particularly large for

the 6-21G** (5D) basis set used in the CRYSTAL calculations. However, after

correction, the interaction energies of the clusters for this basis that became

approximately equal to those calculated using the other methods.

No geometric optimizations were attempted for several reasons: (a) We wish to evaluate the interactions at the experimental geometry; (b) The large basis set superposition errors (BSSE) and consequent counterpoise corrections would be expected to adversely affect the reliability of the potential energy surface.[10]

3.2 Benzoquinone cluster calculations

The interaction energies for clusters containing up to seven benzoquinone molecules calculated five different ways are collected in Table 3.1. To simplify our discussion, we will use the B3LYP/D95* calculated values where individual energies are cited. These seem appropriate as they allow for electron correlation and are in reasonable agreement with three of the other methods, while the B3PW91 results seem to differ.

The energy of an individual hydrogen bond was taken as that of the **AB** dimer (see Figure 3.1), this being the only dimer containing only one hydrogen bond. The stabilization energy of 0.97 kcal/mol is consistent with other calculations on C-H...O interactions of this type. The results of the calculations on the **AC** dimer and other aggregates suggest that H bond cooperativity plays an important role in the crystal interaction energy. We approximated the cooperativity of each aggregate calculated using GAUSSIAN 94 by subtracting the appropriate number of individual hydrogen bond energies from the total interaction energy. Within the planar structure depicted

in Figure 3.1, one can trace several kinds of cyclic hydrogen bonding interactions.

One kind of ring involves two molecules, each providing hydrogen bonding donor and

an acceptor. Molecules **A** and **C** form such a cycle. These hydrogen-bonding rings

contain eight atoms and six π-electrons in a ring and provides the proper polarization

(alternating positive and negative) in the σ-system. A second kind of ring involves

three molecules. Molecules **A, B** and **C** form such a ring. Here, one molecule, **A**,

provides two acceptors, the second molecule, **B**, provides a donor and an acceptor

while the third molecule, **C**, provides two donors within the H-bonding ring. These H-

bonding rings also contain 6 π-electrons, but do not provide the proper polarization

(alternating positive and negative) in the σ-system as they contain an odd number of

atoms (nine). Consequently, the **AC** ring leads to a much larger cooperative interaction

than the **ABC** ring. Each aggregate composed of 3 or more molecules that contain an

ABC ring must also contain at least one **AC** type ring. The cooperativity due to the

ABC ring can be estimated as the difference between the total cooperativity in **ABC**,

less the cooperativity of the **AC**-ring. The data in Table 3.1 indicate the total **ABC**-

ring cooperativity (-0.13 kcal/mol) to be about 10% of the **AC**-cooperativity (-1.55

kcal/mol). Inspection of Figure 3.1 leads to identification of larger H-bonding rings

(each of which contains one or more of the smaller ones).

Aside from the **ABC** aggregate discussed above, two other trimers are

identifiable from Figure 3.1: **FAC** and **EAB**. **FAC** contains two **AC** interactions. The

central molecule, **A**, is polarized opposite of its two partners: **C** and **F**. As a result, the

additional cooperativity in the **FAC** aggregate (as compared to two **AC**-s) is negligible

(-0.05 kcal/mol). The **EAB** aggregate is destabilized slightly (+0.05 kcal/mol) relative to two **AB** interactions. The likely cause for this is a repulsive interaction of 0.04 kcal/mol (Table 3.1) between molecules **B** and **E** (due to their relative orientations) combined with the uncooperative polarization of the central molecule, **A**. As there are no cyclic H-bonding structures in **EAB**, no aromatic stabilization is possible.

Table 3.1. Energies of benzoquinone clusters calculated using GAUSSIAN 94 (kcal/mol).

M[a]	HB[b]	Type[c]	HF			B3LYP	B3PW91	MP2
			AM1	6-21G**5D		D95*		
			Energy of interaction					
2	2	AC	-3.01	-3.03	-3.40	-3.49	-2.65	
	1	AB	-1.06	-0.71	-0.79	-0.97	-0.38	
	0	A'A						-0.73
	0	A'D						-1.62
	0	BE	0.03	0.04	0.06	0.04	0.04	
3	4	FAC	-6.07	-6.19	-6.90	-7.03	-5.36	
	2	EAB	-2.06	-1.27	-1.45	-1.89	-0.74	
	2	GAD	-2.03	-1.17	-1.36	-1.82	-0.67	
	4	ABC	-5.18	-4.61	-5.01	-5.56	-3.60	
4	7	ABCG	-9.31	-8.49	-9.18	-10.00	-6.71	
	6	ABCD	-7.54	-6.65	-7.08	-8.13	-5.04	
7	16	ABCDEFG	-21.16	-19.51	-20.85	-23.23	-15.48	
			Total cooperative interaction					
2	2	AC	-0.88	-1.61	-1.82	-1.55	-1.89	
	1	AB	0.00	0.00	0.00	0.00	0.00	
3	4	ACF	-1.81	-3.35	-3.73	-3.15	-3.84	
	2	ABE	0.07	0.15	0.13	0.05	0.02	
	2	ADG	0.09	0.25	0.22	0.12	0.09	
	4	ABC	-0.93	-1.77	-1.84	-1.68	-2.08	
4	7	ABCG	-1.86	-3.52	-3.63	-3.21	-4.05	
	6	ABCD	-1.16	-2.39	-2.33	-2.31	-2.76	
7	16	ABCDEFG	-4.14	-8.15	-8.16	-7.71	-9.40	
			Estimate of infinite sheet energy from aggregate					
	total		-5.44	-5.30	-5.44	-6.19	-4.33	
Cooperative component			-1.19	-2.46	-2.26	-2.31	-2.81	

[a]number of molecules in aggregate [b]number of H-bonds in aggregate [c]See Figure 3.1.

The total cooperative contribution to the seven-molecule aggregate (-7.71

kcal/mol) is roughly one-third the total interaction energy (-23.23 kcal/mol), about

10% more than would be expected from adding the cooperative contributions from

each of the dimers (-6.98 kcal/mol). We estimate the stabilization energy of an

individual molecule in an infinite sheet from the heptamer (-6.19 kcal/mol) by

subtracting the stabilization due to the eight H-bonds (two **AC** rings and four H-bonds)

that do not involve the central molecule, then dividing by two (as each hydrogen bond

involves two molecules). The cooperative contribution is 37% (-2.31 kcal/mol).

3.3 Benzoquinone periodical calculations

The results of periodic calculations on infinite chains, slabs, and the three

Table 3.2. Periodic calculations using CRYSTAL95 at the HF/6-21G** level. Cluster
calculations using trimers in place of infinite chains with the same basis set are
included for comparison.

	Periodic calculation			Aggregate calculation	
Chains	Uncorrected	CP-corrected	using MP2/D95** dimeric **A'D** and **A'A**	uncorrected	CP-corrected
ACF	-8.71	-3.35		-8.73	-3.35
ABE	-3.13	-0.85		-1.20[a]	-0.20[a]
ACF + 2 **ABE**	-14.97	-5.05		-10.13	-3.75
2D-slab	-15.20	-5.49		-15.49	-5.30
Stack **A'D**	-0.34	+1.78	-1.62		
Stack **A'A**	-0.64	+0.18	-0.73		
all chains	-16.28	-1.31			
3D-crystal	-15.17	-0.93	-9.46[b]		

[a]The average of **ABE** and **ADG** from table 1. [b]The MP2/D95* values for the dimers replace the two
stack **A'D** and stack **A'A** periodic HF calculations and are added to the corrected slab interaction.
dimensional crystal are collected in Table 3.2. Due to limitations in the CRYSTAL

programs, we were constrained to work at the HF/6-21** level, using five d-orbitals
(rather than the six used in the more common gaussian basis sets). Individual (finite)
aggregates were calculated using this procedure for comparison with the periodic
calculations. In the following discussion, all energies (including the cluster
calculations that are used for comparison) refer to the values obtained using this
procedure. The large CP corrections required to offset the BSSE have complicated the
analysis of these calculations. In many cases, the CP correction accounts for more than
half the (uncorrected) interaction energy. The fact that the CP-corrections are so large
combined with the substantially different procedures necessary for calculating CP in
CRYSTAL makes comparisons somewhat difficult.

In the crystal structure, one can identify four different types of chains formed
by the nearest neighbors in the benzoquinone crystal: two within the planar sheet
(formed by molecular contacts of **AB** and **AC** type), and two involving molecules in
adjacent sheets (stacking interactions). The different stacking interactions (Figure 3.2)
involve interactions of the type **A-D** (smmetrically equivalent to **A-E**) and **A-A**. The
stabilization/molecule of infinite chain **AC** before CP correction shows no additional
cooperative effect beyond the stabilization of the dimer (8.7 kcal/mol for both), but
roughly 10% additional cooperativity after CP correction (3.3 vs. 3.0 kcal/mol). This
result is consistent with the discussed above small additional cooperativity of the **FAC**
aggregate with respect to the two **AC**-s. The interaction energy per hydrogen bond of
chain **AB** is less than for the dimer (-3.1 vs. -3.3 kcal/mol) before CP correction. This
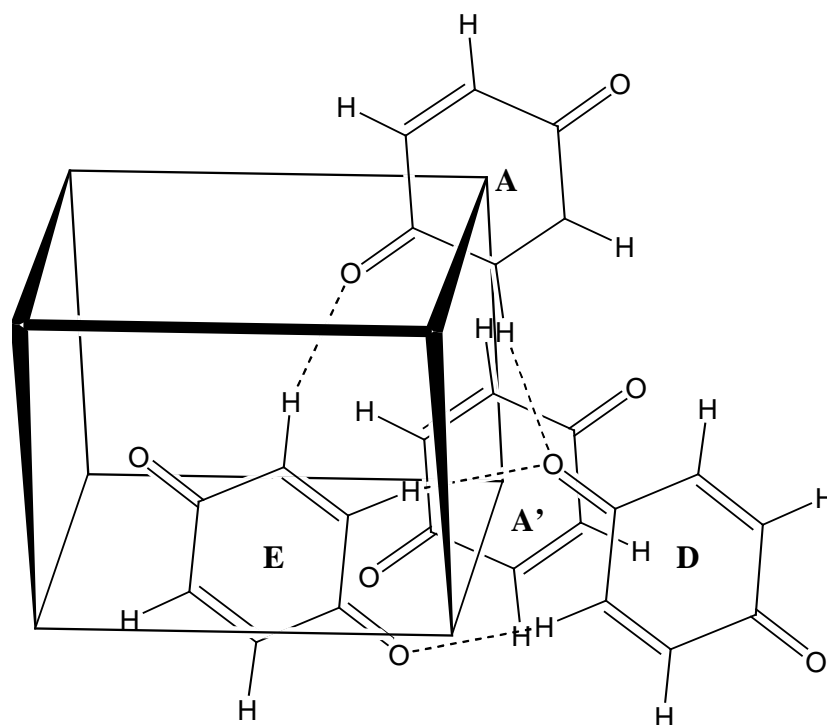
Figure 3.2. Four molecules forming stacking interactions in the experimental crystal structure of *para*-benzoquinone. Molecules **A**, **D** and **E** correspond to the same molecules in Figure 3.1. Molecule **A'** corresponds to a molecule equivalent to **A** in a plane behind that of **A**, **D** and **E**.

appears to be consistent with the calculation of the **EAB** aggregate (discussed above), where the interaction was slightly less than that of two **AB**s. However, unlike the **BE** interaction which is repulsive, the **CF** interaction should be attractive. The chains that involve stacking interactions, **A·D** and **A·A**, have interaction energies of -0.34 and -0.64 kcal/mol, respectively. However, they both become repulsive after CP-correction (see Table 3.2). The sum of interaction energies over in-plane chains (taking into account that each molecule participates in one **AC** and two **AB** chains) is -15.0 kcal/mol before CP correction to be compared to -15.2 kcal/mol interaction energy per molecule of the infinite sheet. Nonadditivity of the CP correction makes BSSE

corrected values difficult to compare. The sum over all chains leads to the total

stabilization of 16.28 kcal/mol vs. 15.20 kcal/mol for the 3D structure. The apparent

negative cooperative effect could be due to repulsive 1-3 interactions between

molecules in different chains as well as the non-additivity of the BSSE.

Stabilization of the double infinite sheet is 15.20 before and 5.49 kcal/mol

after CP-correction, as calculated by this method. Thus, the sheets do not interact

before CP correction, but repel each other by 3.74 kcal/mol after correction. The

crystal stabilization after CP correction (0.9 kcal/mol) is consistent with the facts that

each sheet has two neighbors in 3D-structure and that there should be a repulsive

interaction between every second sheet. Clearly, the repulsion between adjacent sheets

must be an artifact of the calculation. There are several reasons for this repulsion: (1)

the intermolecular distances were not optimized for this basis set and fell into a

repulsive region of the potential curve; (2) the basis set gave large BSSE; (3) the HF

method systematically underestimated dispersion energy, which were important for π-π

stacking interactions. MP2/D95* calculations give stacking interactions between

sheets that are attractive by 3.97 kcal/mol (two **A≈D** interactions of -1.62 and one **A≈A**

interaction of -0.73 kcal/mol). If this stacking interaction is used to replace the 3.74

kcal/repulsion, the crystal interaction becomes -9.46, instead of -0.93 kcal/mol.   In

any case, we can conclude that stacking interaction between the sheets in the crystal

are weaker then the H-bonding interactions. This is consistent with weak stacking

energy.

For the discussion of stacking interactions it is useful to mention a recent work

on the dimer of *para*-benzoquinone and pyridine.[11] MP2 calculations overestimated

the stability of the stacking interactions before BSSE. Only after CP correction of the

MP2 energy, did the (experimentally observed) planar H-bonding interactions become

more stable than the stacking interactions. The best stacking interaction (before

vibrational correction) for benzoquinone/pyridine was reported to be 3.06 kcal/mol, or

about twice the apparent stacking in benzoquinone crystals as estimated above. The

calculations using HF or DFT methods show no stability for stacking of benzoquinone

and pyridine. This is no surprise, as interactions that are often attributed to dispersion

forces or time-dependant polarization are poorly treated by HF calculations. This effect

occurs for both H-bonds and stacking interactions but is hidden by much stronger

(usually) electrostatic components of H-bonds. If one neglects multipole/multipole

interactions, the stacking interaction between two nonpolar molecules at HF level

might be close to zero. DFT methods also have not been successful in calculating

dispersion interactions.

The experimental heat of sublimation for benzoquinone has been reported as

15.0 ± 0.8 kcal/mol.[12] This value is close to the uncorrected three dimensional periodic

value calculated by CRYSTAL and is about 1.5 times greater then the most reasonable

(corrected) calculated interaction energies. This overestimation holds even if one

replaces the repulsive stacking interactions with the attractive MP2/D95* values for

the **A=D** and **A=A** dimers, which leads to a crystal energy of 9.46 kcal/mol. If one

estimates the stacking interaction to be about 3 kcal/mol from benzoquinone/pyridine

stacking value, the calculated sublimation energy for benzoquinone becomes about 8.5

kcal/mol, a slightly lower value. One might assume that this value might become somewhat greater if one used the B3PLYP procedure instead of HF/6-21G**. The B3LYP calculation of the stabilization in the seven molecule aggregate is 17% greater than that calculated by HF/6-21G** for the same system. Applying this correction to the CRYSTAL slab calculation and using the MP2/D95* values for the stacking stabilization would yield an estimate of 10.4 kcal/mol for the heat of sublimation. These calculated interactions do not include vibrational corrections or relaxation of the geometry of the crystal to that of the monomer or the PΔV work done upon sublimation. The AM1 calculations performed for comparison gave results for the individual interactions that are similar to the *ab initio* aggregate values, although the cooperative components are somewhat lower.

3.4 Comparison of cluster and periodical calculations

Calculations using various *ab initio* and semiempirical methods gave similar results for the hydrogen bonds within aggregates containing up to seven p-benzoquinone molecules taken from the experimental crystal structure.

The disaccord between the experimental and theoretical results might be due to one or more of several factors: (1) The cooperative component of the crystal interactions might be poorly approximated by the CRYSTAL calculations. (2) The estimate of the stacking interaction or its cooperativity might be inadequate. To the extent that MP2 calculations on the dimer are used, no cooperativity is taken into

account. (3) There may be errors in the experimentally determined heat of sublimation. Nevertheless the individual C-H...O hydrogen bonding energies are in accord with those previously reported for other systems.

Cooperativity accounts for approximately half the interaction energy of the heptamer aggregate. Since the capacity for cooperativity will be greater in the infinite 3D crystal, the cooperative component must be somewhat greater than that calculated for this aggregate.

3.5 Crystal orbital HF calculations on urea and thiourea in experimental geometry

In order to analyze cooperative effects in crystals of urea and thiourea (Figure 3.3), we carried out periodical HF calculations in the experimental geometry. The results are summarized in Table 3.3.
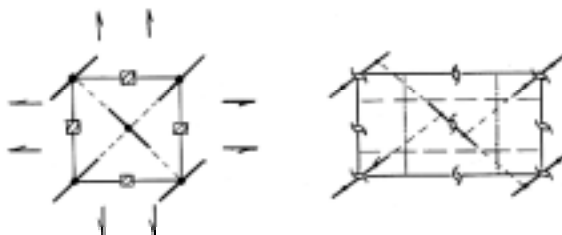

Figure 3.3. The schematic representation for tetragonal *P-42m* (left) and orthogonal *Pmna* (right) crystal structures considered for urea and thiourea.

Table 3.3. Results for single-point 1,2,3D-periodical HF/6-311G** calculations on tetragonal urea and orthogonal thiourea in experimental geometry. Total energy in hartree, interaction energy (molecular relaxation is not included), and counterpoise correction CP in kcal/mol.

	E_{tot}	ΔE	ΔE_{cp}, 2.5A	ΔE_{cp}, 3.0A	ΔE_{cp}, 3.5A	ΔE_{cp}, 4.0A	cp 4.0A
			Tetragonal urea				
AB	-448.098968	-10.72	-9.44	-8.99	-8.97	-8.92	0.90
Z (**CAB**)	-224.065174	-15.21	-14.16	-13.82	-13.77	-13.72	1.49
2Z	-448.135170	-16.72	-14.62	-14.18	-13.88	-13.81	2.91
AD	-448.094288	-7.78	-6.69	-6.42	-6.32	-6.27	0.76
X (**EAD**)	-448.103135	-6.67	-5.57	-5.29	-5.20	-5.15	1.52
XY	-448.127326	-14.26	-14.26	-11.53	-11.38	-11.03	3.23
XZ	-448.136808	-17.23	-14.46	-14.00	-13.53	-13.41	3.82
XYZ (3D)	-448.151783	-21.93	-17.76	-17.19	-16.24	-16.12	5.81
3D, 6-21G**	-447.681065	-33.29	-20.99	-18.27	-16.44	-16.30	17.00
			Orthogonal thiourea				
AB	-1093.382983	-9.94		-9.49	-9.33	-9.31	0.64
AF	-1093.378284	-6.99		-6.41	-6.23	-5.93	1.07
AD	-1093.373880	-4.23		-4.23	-4.08	-3.99	0.24
XYZ (3D)	-2186.821710	-13.72		-12.43	-11.39	-11.03	2.69

Previously reported HF calculations by Dovesi, Roetti et al.[13] on urea crystal were done with the small basis set 6-21G** resulting in high BSSE. We used a 6-311G** basis set to minimize this error. Since basis with low exponential values lead to convergence problems, we had to modify standard 6-311G** by increasing the outermost exponent of SP-functions for the carbon atom from 0.18 to 0.22. Similar modification of the 6-31G** basis set for the periodical calculations were used by Abramov, Coppens et al.[14] They changed the outermost exponents for both C and H atoms to 0.20. In our case, this modification also improved convergence but it resulted in bigger increase in total energy; besides, there was a deviation of the basis set on H atom from the optimum value could affect H-bonding. That is why we preferred to

modify the exponent on the C atom only. After this modification, the convergence was stable. Since full counterpoise correction is impossible for an infinite system, we had to limit the number of ghost atoms used in CP correction to all atoms located at the distance closer than the fixed distance from any atom of the molecule. We used four distances in the range from 2.5 to 4.0 Å. The distance of 3.5Å was found sufficient, as the CP value did not change by more then 0.2 kcal/mol upon further increase.

Total cohesion energy for the urea crystal was found 16 kcal/mol (22 kcal/mol before CP correction). For the 6-21G** basis set, this value is 16.3 kcal/mol, which agrees with the bigger basis set but differs from the value of 21.5 kcal/mol previously reported by Dovesi, Roetti et al.,[13] because of incomplete CP correction in their paper. After adding molecular relaxation and pyramidalization energy (5.00 and 1.51 kcal/mol, obtained by geometry minimization using GAUSSIAN98 and the modified 6-311G** basis set) the energy is 9.5 kcal/mol, two times less then experimental enthalpy of sublimation. For the thiourea crystal after molecular relaxation (1.52 kcal/mol) and piramidalization (0.03 kcal/mol) the cohesion energy is 10 kcal/mol, also about a half of the experimental value. Underestimation the heat of formation in the periodical HF calculations was reported by Abramov, Coppens et al.[14] We should note, that calculated energy does not include zero-point vibration correction and is not directly comparable with enthalpy.

As one can see from the crystal structure (Figure 3.4), urea forms H-bonds with 2 neighbors within the chain (**AB** dimer, 9 kcal/mol) and with 4 neighbors from antiparallel chains (**AC** dimers, 6.6 kcal/mol). The sum of dimeric interactions yields
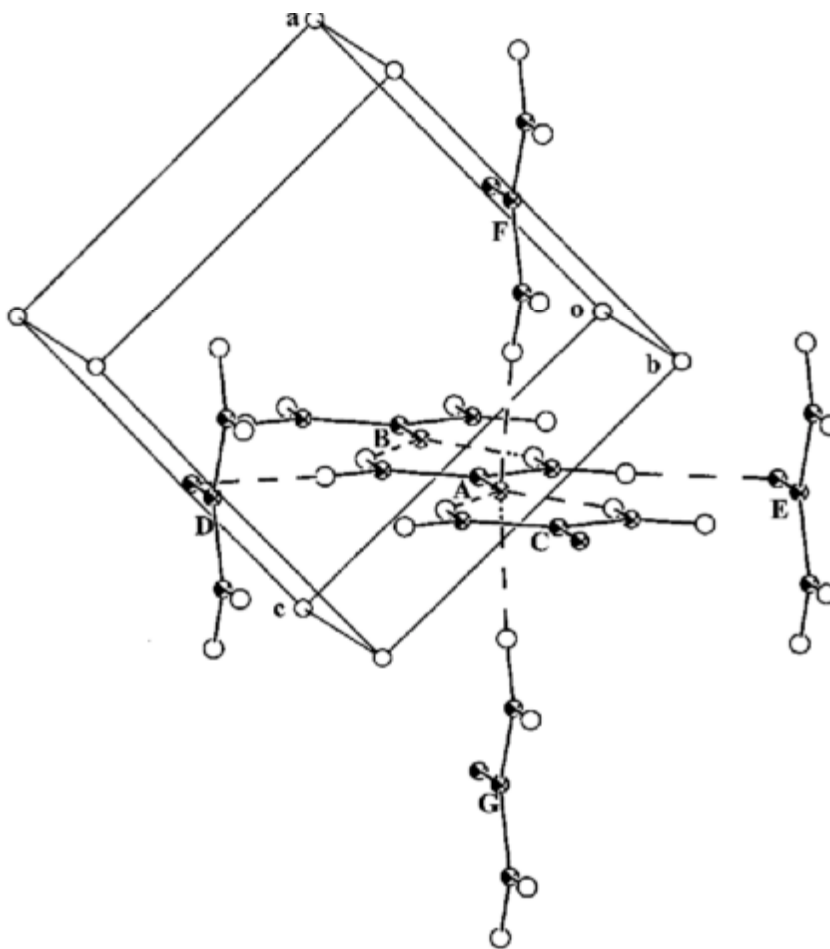
Figure 3.4. H-bonds between central molecule **A** and its nearest neighbors (**B-G**) in experimental crystal structure of urea.

22.2 kcal/mol, more than twice the result of 3D-calculation. For the thiourea (Figure

3.5) crystal sum of dimeric interactions **AB**, **AD**, and **AF** (9.3, 4 and 6 kcal/mol) is

19.3 kcal/mol, also twice of the periodical result. However, we did not include (often

repulsive) second-neighbor interactions in this estimate and neglected all cooperative

effects.
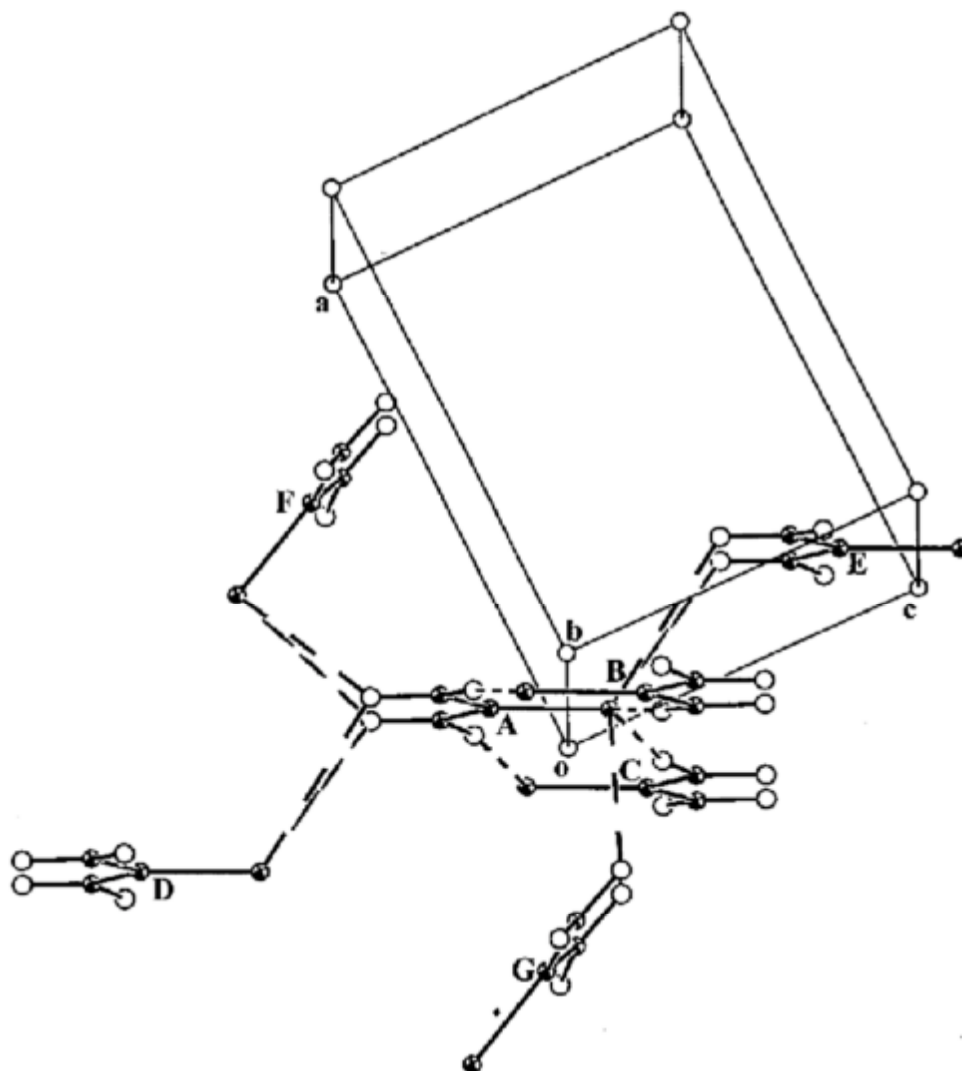
Figure 3.5. H-bonds between central molecule **A** and its nearest neighbors (**B-G**) in experimental crystal structure of thiourea.

We can also consider non-additive effects in different directions in the urea crystal. In Z-direction, H-bond energy increases more then 50% from dimer **AB** (9 kcal/mol) to an infinite chain (13.7 kcal/mol). Addition of an antiparallel chain stabilizes the system by only 0.1 kcal/mol (1.2 kcal/mol before CP correction), despite

the formation of one new H-bond of **AD** type per two molecules. This is due to repulsion between the molecules of antiparallel chains.

Similar weakening of H-bonds was found in periodical HF/6-31G** calculations of ice VIII.[15] Ice structure is a superposition of two 3D-networks of water molecules with opposite dipole moments. When these substructures are combined, electrostatic repulsion between molecules included into the different substructures results in the weakening of H-bonds.

An infinite layer of molecules in the XZ plane is slightly destabilizing with respect to isolated chains after CP correction (and 2 kcal/mol stabilizing before CP correction). The energy of the isolated H-bond in X-direction also decreases from 6.6 kcal/mol in **AD** dimer to 5.2 kcal/mol in the infinite chain. The formation of a second equivalent H-bond in Y-direction stabilizes the XY-layer so that is slightly cooperative with respect to X-chain (1 kcal/mol). As a result the 3D-structure is 3.5 kcal/mol more stable than the single chain in Z-direction, even though each molecule forms two H-bonds of **AD** type.

We should also mention, that part of non-additivity of intermolecular interaction comes from non-additivity in CP correction. The last column in Table 3.3 reports our best estimate for average CP correction per molecule in infinite structures and in dimers calculated with the same cutoff limit of 4 Å. Note that for the dimers the actual correction is twice the reported value. One can see for the Z-chain CP correction is 26% less then sum of corrections for **AB** and **AC** pairs, whereas for X-chain it is exactly equal to the sum for **AD** and **AE** pairs. This is because the addition of the

ghost **C** does not improve the wavefunction for **A** in the presence of ghost **B** as efficiently as ghost **B** did. On the other hand, CP correction for the layer XY is 6% greater then sum of two chains in X and Y directions. Similarly, CP correction for the 3D-structure is 22% greater than sum of the chains in X, Y, and Z directions due to the presence of additional ghosts in 2D- and 3D-structure corresponding to diagonal second-neighbors, which were not present in either of the chains.

3.6 Semiempirical optimizations of urea and thiourea tetragonal and orthogonal crystal structures

The application of single-point calculations to hypothetical polymorphic forms is complicated by their unknown geometry. Although the structures for the tetragonal forms of urea and orthogonal thiourea are known (see Figures. 2.3, 2.7, and 3.3), the second polymorph is hypothetical. Therefore, crystal structures of orthogonal urea and tetragonal thiourea must be qualitatively estimated.

A priori prediction of possible crystalline forms for urea and thiourea was recently performed[16] using the POLYMORPH module of the Cerius^2 package, commercially available from MSI. Dreiding force field[17] and rigid intramolecular experimental geometry were used. Atomic charges were obtained by fitting to molecular electrostatic potential distribution obtained in MNDO calculations. The search was restricted to five space groups (*P2$_1$/c, P-1, P2$_1$2$_1$2$_1$, P2$_1$, C2/c*) with one symmetrically independent molecule. These space groups cover 70% of the molecular

structures in the Cambridge Database. In some cases, the structure spontaneously adopted higher symmetry. The local minima found in this search correspond to possible polymorphic modifications. Atomic coordinates for the ten solutions of the lowest energy are listed in Table 3.4. For urea, tetragonal structure was correctly found to be the most stable, and orthogonal structure was among the the low-energy polymorphs. For thiourea, the experimental orthogonal structure was not the most stable, and tetragonal structure was not present among low-energy solutions. Presumably, the reason for this failure was inaccuracy in the parameters of the additive force field.

We applied the semiempirical MO methods to predict the geometry of orthogonal urea and tetragonal thiourea and compared their stability to the stability of the experimentally observed structures. The periodical MO method with semiempirical AM1[18] Hamiltonian as coded in MOPAC 6 (adapted[19] for Windows NT) was used. Although only 1D- (polymer) capability is described in the manual, we have found that this package gives reasonable results in all three dimensions for the test examples.

The tetragonal structure of urea (described in Section 2.8) was modified. To overcome inaccuracy of one-point Brillouin zone integration, translation vectors should have values over 5 Å (as suggested in the MOPAC manual). For this purpose ,diagonal ($a=a+b$, $b=a-b$) coordinate transformation was applied to convert the experimental tetragonal unit cell of $P\text{-}42_1m$ symmetry containing two molecules to a supercell of $Cmm2$ symmetry containing four molecules, and parameter c was doubled. Consequently, the new unit cell contained four chain dimers, arranged in a cyclic

Table 3.4a. Space groups (number and axis setting option are given according to International Tables of Crystallography), optimized with Dreiding force field unit cell parameters and atomic fractional coordinates for ten the most stable structures, as predicted by Cerius2/POLYMORPH for urea.

	4 P 21		opt 1		14 P 21/c		opt 2		14 P 21/c		opt 2
abc	4.662	5.230	5.230	abc	5.208	5.208	10.687	abc	9.394	6.906	3.433
	90	90	90		90	119.166	90		90	90.004	90
N1	-0.3266	-0.1548	0.3880	N1	0.5536	0.1114	1.1650	N1	0.3894	0.3944	0.8061
C2	-0.1718	-0.0168	0.2500	C2	0.3373	0.2500	1.0873	C2	0.3118	0.2500	0.7500
N3	-0.3266	0.1212	0.1120	N3	0.2765	0.3886	1.1650	N3	0.3894	0.1056	0.6939
O4	0.0909	-0.0168	0.2500	O4	0.2061	0.2500	0.9561	O4	0.1815	0.2500	0.7500
H5	-0.2336	0.2350	-0.0018	H5	0.1163	0.5033	1.1196	H5	0.3463	-0.0141	0.6266
H6	-0.5281	0.1045	0.1287	H6	0.3943	0.3714	1.2656	H6	0.4892	0.1253	0.7169
H7	-0.2336	-0.2686	0.5018	H7	0.6229	-0.0033	1.1196	H7	0.3463	0.5141	0.8735
H8	-0.5281	-0.1381	0.3713	H8	0.6370	0.1286	1.2657	H8	0.4892	0.3747	0.7831

	14 P 21/c		opt 1		14 P 21/c		opt 2		14 P 21/c		opt 2
abc	3.89	8.745	8.159	abc	6.95	6.655	6.465	abc	4.675	13.317	3.891
	90	118.471	90		90	84.496	90		90	78.404	90
N1	0.3433	0.1464	0.1081	N1	0.5554	0.1657	0.3560	N1	0.8523	0.6846	0.0767
C2	0.4145	0.0694	0.2500	C2	0.5495	0.2988	0.2206	C2	0.6706	0.6176	0.1974
N3	0.6272	0.1464	0.3919	N3	0.3877	0.3829	0.2425	N3	0.8092	0.5471	0.3012
O4	0.2835	-0.0580	0.2500	O4	0.6787	0.3394	0.0847	O4	0.4041	0.6205	0.2335
H5	0.6956	0.1039	0.5105	H5	0.3649	0.4836	0.1444	H5	0.7085	0.4904	0.4113
H6	0.6990	0.2455	0.3723	H6	0.2974	0.3383	0.3523	H6	1.0147	0.5551	0.2666
H7	0.1746	0.1039	-0.0105	H7	0.6670	0.0836	0.3543	H7	0.7882	0.7448	-0.0144
H8	0.4545	0.2455	0.1277	H8	0.4444	0.1531	0.4520	H8	1.0504	0.6719	0.0857

	14 P 21/c		opt 2		14 P 21/c		opt 1		14 P 21/c		opt 2
abc	4.684	3.809	13.619	abc	4.657	7.003	6.917	abc	10.002	6.906	3.434
	90	72.601	90		90	86.228	90		90	69.922	90
N1	0.7453	0.2924	0.0488	N1	1.2831	0.3954	0.1122	N1	0.3894	0.1056	1.3046
C2	0.5221	0.2023	0.1210	C2	1.1282	0.2500	0.1047	C2	0.3118	0.2500	1.4382
N3	0.6117	0.0761	0.1915	N3	1.2831	0.1047	0.1122	N3	0.3894	0.3944	1.4167
O4	0.2613	0.2483	0.1235	O4	0.8725	0.2500	0.0737	O4	0.1815	0.2500	1.5685
H5	0.4675	-0.0099	0.2513	H5	1.1982	-0.0163	0.0910	H5	0.3463	0.5141	1.5272
H6	0.8215	0.0738	0.1813	H6	1.4830	0.1245	0.1242	H6	0.4892	0.3747	1.2939
H7	0.7160	0.4012	-0.0100	H7	1.1982	0.5163	0.0910	H7	0.3463	-0.0141	1.2803
H8	0.9356	0.2559	0.0583	H8	1.4830	0.3755	0.1242	H8	0.4892	0.1253	1.2278

	14 P 21/c		opt 2
abc	7.685	7.691	4.726
	90	89.037	90
N1	0.2672	0.3340	0.8207
C2	0.3676	0.2128	0.8845
N3	0.3092	0.1349	1.0988
O4	0.5004	0.1731	0.7541
H5	0.3754	0.0390	1.1644
H6	0.2061	0.1798	1.1852
H7	0.2969	0.4005	0.6584
H8	0.1663	0.3505	0.9367

Table 3.4b. Space groups (number and axis setting option are given according to International Tables of Crystallography), optimized with Dreiding force field unit cell parameters and atomic fractional coordinates for ten the most stable structures, as predicted by Cerius2/POLYMORPH for thiourea.

	14 P 21/c		opt 2		14 P 21/c		opt 2		14 P 21/c		opt 1
abc	11.613	7.334	3.929	abc	5.458	3.775	15.796	abc	5.483	7.679	7.763
	90	70.229	90		90	108.804	90		90	69.117	90
N1	0.3410	0.3836	0.7826	N1	0.2536	1.2232	0.0517	N1	1.2459	0.1073	0.6134
C2	0.4046	0.2500	0.8455	C2	0.4485	1.2948	0.1226	C2	1.1208	0.2500	0.6090
N3	0.3410	0.1164	1.0355	N3	0.3876	1.3906	0.1923	N3	1.2459	0.3927	0.6134
S4	0.5601	0.2500	0.6899	S4	0.7606	1.2652	0.1240	S4	0.8158	0.2500	0.5996
H5	0.3833	0.0131	1.0871	H5	0.5237	1.4539	0.2463	H5	1.1682	0.5040	0.6058
H6	0.2533	0.1248	1.1239	H6	0.2080	1.4007	0.1879	H6	1.4157	0.3842	0.6227
H7	0.3833	0.4870	0.6463	H7	0.2858	1.1535	-0.0025	H7	1.1682	-0.0040	0.6058
H8	0.2533	0.3752	0.8695	H8	0.0818	1.2418	0.0552	H8	1.4157	0.1158	0.6227

	14 P 21/c		opt 2		14 P 21/c		opt 2		14 P 21/c		opt 1
abc	5.495	14.96	4.051	abc	4.052	14.96	5.499	abc	5.495	14.961	4.051
	90	68.434	90		90	111.679	90		90	111.56	90
N1	1.3245	0.0542	0.3094	N1	0.8661	0.9459	0.1755	N1	0.9025	0.3195	0.4774
C2	1.2322	0.1185	0.1739	C2	1.0938	0.8816	0.2678	C2	0.7322	0.3816	0.3261
N3	1.4026	0.1805	0.0226	N3	1.0748	0.8195	0.0974	N3	0.8245	0.4459	0.1907
S4	0.9167	0.1215	0.1971	S4	1.3862	0.8785	0.5833	S4	0.4167	0.3785	0.3029
H5	1.3541	0.2314	-0.0843	H5	1.2302	0.7686	0.1459	H5	0.7136	0.4944	0.0676
H6	1.5773	0.1746	0.0211	H6	0.9017	0.8254	-0.0773	H6	1.0046	0.4427	0.2142
H7	1.2136	0.0056	0.4324	H7	0.8539	0.9944	0.2864	H7	0.8540	0.2686	0.5843
H8	1.5046	0.0573	0.2859	H8	0.7095	0.9427	-0.0046	H8	1.0773	0.3254	0.4790

	14 P 21/c		opt 1		14 P 21/c		opt 1		14 P 21/c		opt 2
abc	5.368	8.263	7.178	abc	5.416	13.636	4.617	abc	8.401	9.453	4.013
	90	71.023	90		90	114.279	90		90	98.591	90
N1	0.8768	0.0906	0.6888	N1	0.2527	0.9263	0.1474	N1	0.4266	0.3619	0.8212
C2	0.9144	0.2418	0.6378	C2	0.4593	0.8812	0.1348	C2	0.5602	0.2966	0.7942
N3	1.1519	0.2830	0.5314	N3	0.4084	0.8331	-0.1263	N3	0.5623	0.1642	0.8819
S4	0.6661	0.3801	0.7057	S4	0.7720	0.8808	0.4395	S4	0.7182	0.3789	0.6560
H5	1.1851	0.3926	0.4857	H5	0.5522	0.7970	-0.1502	H5	0.6546	0.1060	0.8634
H6	1.2921	0.2046	0.4932	H6	0.2285	0.8348	-0.2931	H6	0.4686	0.1275	0.9630
H7	0.7008	0.0538	0.7579	H7	0.2747	0.9651	0.3309	H7	0.4132	0.4595	0.7528
H8	1.0242	0.0173	0.6601	H8	0.0802	0.9205	-0.0308	H8	0.3423	0.3104	0.9059

	19 P 21 21 21		opt 1
abc	8.307	5.614	6.73
	90	90	90
N1	0.1771	0.8616	0.2449
C2	0.1083	0.8397	0.0726
N3	0.0349	1.0255	0.0021
S4	0.1178	0.5814	-0.0580
H5	-0.0166	1.0150	-0.1258
H6	0.0340	1.1734	0.0748
H7	0.2352	0.7272	0.2985
H8	0.1724	1.0105	0.3160

herringbone cluster.

The orthogonal structure of *Pmna* symmetry with four molecules in the unit cell was taken from the experimental crystal structure of thiourea, described in Section 2.9 (see Figure 2.6). The notations were rearranged (*a=c, b=a, c=b*) so that the ribbons were parallel to Z-directions, like the chains in the tetragonal structure. We constrained the molecules to planarity, which is not imposed by symmetry in this structure. We also constrained the ribbons to be planar by changing the NCS...S dihedral from 5.6^o to 0°. The unit cell consists of two cyclic dimers, forming one herringbone H-bond between them. The C=S...S and S...S=C angles along this H-bond are flexible, so that optimization of these values for clusters, layers and ribbons distorts them considerably. For instance, optimization of the cluster representing one unit cell changes the values from 17° and 70° observed in crystal to 3° and 178° in the cluster. Instead of fixing these angles at their experimental values, we idealized them to 0° and 90°, so that the planes of the ribbons were orthogonal to each other. Both changes were achieved by 17° rotation of the symmetrically independent molecule about the crystallographic Z-axis. We will refer to the new structure as an idealized orthogonal structure. The experimental and idealized structures are shown side by side in Figure 3.6.

The energies of experimental and optimized structures are presented in Table 3.6. We should mention, that optimization slightly changes the crystallographic parameters from *a* 5.485 Å, *b* 7.657 Å, *c* 8.588 Å to *a* 5.305 Å, *b* 7.396 Å, *c* 8.217 Å, and idealization increases them to *a* 6.653, *b* 7.584, *c* 8.217. The unit cell

Figure 3.6. Experimental (left) and idealized (right) molecular packing in orthogonal thiourea.

volume increases from 322 Å^3 to 415 Å^3. According to Kitaigorodskii≡s postulate,[1] the molecules in the crystals are closely packed. This insures a minimum of isotropic components of intermolecular interaction (mostly dispersion attraction). Only in rare cases, when strong directional intermolecular interactions dominate (such as in ice), does the close packing principle fail to hold. Clearly, idealization of orthogonal unit cell contradicts the close packing principle. However, idealization stabilizes the unit cell tetramer by 2 kcal/mol, and the crystal structure by about 6 kcal/mol. This is because the HF method and its semiempirical simplifications give poor description of dispersion interactions.

We have to note that experimental crystal structure is not a local minimum on calculated potential energy. After one subtracts the energy of molecular relaxation, the experimental structure is 3.5 kcal/mol less stable then the structure obtained after the

Table 3.5. Results for optimized and experimental 1,2,3D-periodical AM1 calculations on tetragonal and orthogonal structures of urea and thiourea. Heat of formation ΔH, periodical stabilization of the unit cell ΔH_{int}, and enthalpy of sublimation ΔH_{sub} are in kcal/mol.

	ΔH	ΔH_{int}	ΔH_{sub}	ΔH	ΔH_{int}	ΔH_{sub}	ΔH	ΔH_{int}	ΔH_{sub}	ΔH	ΔH_{int}	ΔH_{sub}
tetragon.	experimental urea			optimized urea			optimized thiourea					
1 mon	-42.93			-44.08			9.89					
1 cell	-372.68	0.00	-3.66	-409.74	0.00	-7.14	6.57	0.00	-9.07			
Z-chain	-404.48	-31.80	-7.63	-435.50	-25.76	-10.36	-25.70	-32.27	-13.10			
X-chain	-382.09	-9.41	-4.83	-420.10	-10.36	-8.43	-1.71	-8.28	-10.10			
XY-layer	-391.51	-18.83	-6.01	-430.49	-20.75	-9.73	-16.45	-23.02	-11.95			
XZ-layer	-411.41	-38.73	-8.50	-446.81	-37.07	-11.77	-32.76	-39.33	-13.99			
3D	-420.66	-47.98	-9.65	-457.45	-47.71	-13.10	-40.64	-47.21	-14.97			
orthog.				optimized urea			optimized thiourea			experimental thiourea		
1 mon				-44.08			9.89			16.9		
1 cell				-197.79	0.00	-5.37	10.05	0.00	-7.38	34.80	0.00	-8.20
Z-chain				-211.14	-13.35	-8.71	-0.20	-10.25	-9.94	13.83	-20.97	-13.44
X-chain				-201.92	-4.13	-6.40	4.02	-6.03	-8.89	18.03	-16.77	-12.39
Y-chain				-202.20	-4.41	-6.47	7.27	-2.78	-8.07	30.59	-4.21	-9.25
D-chain				-200.81	-3.02	-6.12	2.00	-8.05	-9.39	32.42	-2.38	-8.79
XY-layer				-210.18	-12.39	-8.47	-8.78	-18.83	-12.09	9.80	-25.00	-14.45
XZ-layer				-215.11	-17.32	-9.70	-7.68	-17.73	-11.81	0.45	-34.35	-16.79
YZ-layer				-215.11	-17.32	-9.70	-7.68	-17.73	-11.81	10.39	-24.41	-14.30
DZ-layer				-213.58	-15.79	-9.32				13.25	-21.55	-13.59
3D				-219.05	-21.26	-10.68	-23.60	-33.65	-15.79	-4.02	-38.82	-17.91
3D, exp				-217.17	-19.38	-10.21	-18.05	-28.10	-14.40			

optimization for both urea and thiourea.

One can see that the total sublimation energies are underestimated by about 30% AM1 correctly predicts the tetragonal form to be more stable for urea, but incorrectly predicts the tetragonal form of thiourea to be more stable by about 0.5 kcal/mol.

It is also interesting to compare cooperative effects in different directions. In agreement with HF/6-311G** results, the interactions in the tetragonal structure are almost additive in X and Y-directions (the XY layer is twice as stabilizing as the X-

chain), and anticooperative (by about 5%) in X and Z directions. In the orthogonal structure, the X and Y directions are strongly cooperative (25%), additive in Y and Z directions, and 10% anticooperative in X and Z-directions. Discussions of this effect will be presented in Chapters 5 and 7 below.

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